

# PATENT SPECIFICATION

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## NO DRAWINGS

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## (54) IMPROVEMENTS IN OR RELATING TO SEWAGE FLOCCULATION

(71) We, HERCULES INCORPORATED, a corporation organized under the laws of the State of Delaware, one of the United States of America, of 910 Market Street, City of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to sewage treatment, and more particularly to an improved process of removing suspended solids from sewage, at least a portion of which sewage has been subjected to aerobic microbial action (oxidation), which comprises aiding the separation of the solids from the water by contacting the sewage with a flocculating agent.

In a typical sewage treatment plant the steps involved often include, in the order given, (1) primary sedimentation (usually after coarsely screening the raw sewage through grit separators), (2) aeration, (3) digestion, (4) elutriation, (5) vacuum filtration and (6) incineration.

The disclosure that at least a portion of the sewage has been subjected to aerobic microbial action is satisfied e.g. by one or more of the following.

(1) Some or all of a supply of raw sewage having been aerated,

(2) Recirculation to raw sewage (a portion of which, all or none may have been aerated) of one or more streams resulting from treatment of sewage effluent (supernatant overflow) from the primary sedimentation step (secondary solids streams which, by definition, are always aerated); or from subsequent steps (tertiary, etc. solids streams which can be aerated in addition to the aeration to which the secondary solids streams, from which they have been obtained,

The amount of suspended solids present in raw sewage varies widely, e.g. usually about 100—700 p.p.m. dry weight basis by weight of the total sewage. When raw sewage enters a treatment plant, it is generally coarsely screened through grit separators in a preliminary step and pumped to primary sedimentation tanks. The sewage is held in the primary sedimentation tanks until some of the suspended solids settle out by gravity. During this process, suspended particles, agglomerate, shrink, lose some of their water, and ultimately settle. However this gravity settling business is intolerably slow, requiring several hours as compared with only a few minutes for the grit separation. Furthermore far too much of the suspended solids fails to agglomerate and therefore remains suspended. Since the primary sedimentation process is continuous so that raw sewage is continuously pumped into the primary sedimentation tanks, the buildup of unsettled solids rapidly overloads these tanks. This buildup of the suspended solids in sewage is extremely undesirable because it makes it necessary to employ extra steps to reduce the biological oxygen demand of this sewage before it can be discharged into natural streams.

Heretofore several sewage treatment plants have added anionic polyelectrolytes as flocculating and settling aids to the primary sedimentation facilities and thereby reduced the necessary tank "hold" time. This permitted an increase in the influent flow to the primary sedimentation basins without the usual detrimental solids buildup in the influent. This increased the rate of flocculation and the amount of solids recovered. However serious difficulties were encountered in cases where some or all of the raw sewage slurry had been subjected to microbial aerobic action, this difficulty being directly proportional to the percentage of sewage which had been so subjected and to that varying degree destroying or

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electrolytes at all because they did a worse job than using no flocculant (e.g. see Table 3 hereinafter).

- 5 According to the present invention it has been found that the rate at which the suspended solids flocculate and settle out of sewage, at least a portion of which has been subjected to aerobic microbial action, is increased and the amount of suspended solids which flocculate and settle out is increased when a particular polyelectrolyte, an acrylamide-beta methacryloyloxyethyltrimethylammonium methyl sulfate copolymer, is used. This particular cationic copolymer even when used in very small amounts relative to the sewage being treated, effects these desirable results at least in part by increasing the flocculation rate, floc size and floc density and these in turn give a substantially faster sedimentation rate and also an appreciable increase in the per cent solids recovered. The copolymer component, beta-methacryloyloxyethyltrimethylammonium methyl sulfate, is hereinafter designated, for brevity, MTMMS.
- 25 The effectiveness of the particular copolymer used in the present invention as a flocculant in the treatment of sewage at least a portion of which has been subjected to aerobic microbial action has been demonstrated both in the laboratory and in actual practice as experienced in sewage treatment plants.
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The following examples illustrate various

embodiments of the present invention. These examples are not intended to limit the present invention beyond the scope of the appended claims. In these examples and elsewhere herein parts and per cent are by weight unless otherwise indicated.

#### EXAMPLES 1-16

##### *Laboratory Runs*

These runs were carried out to determine the effect of various polymeric flocculating agents on the recovery of suspended solids from aerated raw aqueous sewage.

Aerated raw aqueous sewage containing 350 p.p.m. suspended solids was taken from a sewage treatment plant just after it was aerated and just before it was passed into the primary sedimentation tanks. One liter of this aerated raw sewage was placed in each of several clean 1-liter graduated cylinders. Flocculating agent was then added to the sewage slurry and mixed therewith by inverting the graduated cylinders 10 times, after which the cylinders were allowed to stand for 1 hour. A 50-ml portion of the supernatant was pipetted from each of the graduated cylinders at the 900-ml. mark and filtered through a weighed glass fiber filter paper having a pore size of 1 micron. The filter paper was oven dried 1 hour at 110°C. and reweighed to determine the per cent solids settled.

Further details appear in Table 1 hereinafter.

TABLE 1

## Laboratory Runs

Effect of Various Polymeric Flocculating Agents on  
Suspended Solids Recovery from Aerated Raw Sewage

Ex. No.	Flocculating Agent			Per Cent solids Settled <sup>(b)</sup>
	Name	Type	Amount <sup>(a)</sup>	
1	None	None	None	20
2	Sulfonated Polystyrene <sup>(c)</sup>	Anionic	1.6	55
3	90% Acrylamide—10% Sodium Acrylate	Anionic	0.6	62
4	50% Acrylamide—50% Sodium Acrylate	Anionic	1.0	44
5	96% Acrylamide—4% MTMMS	Cationic	0.5	32
6	96% Acrylamide—4% MTMMS	Cationic	0.10	44
7	96% Acrylamide—4% MTMMS	Cationic	0.50	91
8	96% Acrylamide—4% MTMMS	Cationic	5.00	93
9	83% Acrylamide—17% MTMMS	Cationic	0.05	28
10	83% Acrylamide—17% MTMMS	Cationic	0.10	41
11	83% Acrylamide—17% MTMMS	Cationic	0.50	87
12	83% Acrylamide—17% MTMMS	Cationic	5.00	92
13	60% Acrylamide—40% MTMMS	Cationic	0.05	25
14	60% Acrylamide—40% MTMMS	Cationic	0.10	33
15	60% Acrylamide—40% MTMMS	Cationic	0.50	79
16	60% Acrylamide—40% MTMMS	Cationic	5.00	93

(a) p.p.m. dry weight basis by weight of total sewage treated, added as a 0.01% aqueous solution.

(b) Based on suspended solids conc. of 350 p.p.m. and 1 hr. settling time.

(c) Flocculating agent available commercially as "PURIFLOC A-21". (PURIFLOC is a Registered Trade Mark).

EXAMPLES 17—24  
Sewage Plant Runs

5 These runs were carried out to determine the effect of various polymeric flocculating agents on the recovery of suspended solids from aerated raw aqueous sewage.

Flocculating agent was fed into the sewage

the primary sedimentation tanks. Samples were taken from the effluent (supernatant overflow) from the primary sedimentation tanks and the per cent solids settled determined from these. The sampling time, i.e. the time between addition of the flocculating agent and making the determination, was about 15

TABLE 2  
Sewage Plant Runs  
Effect of Various Polymeric Flocculating Agents  
on Suspended Solids Recovery from Aerated Raw Sewage

Ex. No.	Flocculating Agent			Per Cent Solids Settled <sup>(b)</sup>
	Name	Type	Amount <sup>(a)</sup>	
17	None	None	None	32
18	Sulfonated Polystyrene <sup>(c)</sup>	Anionic	0.92	40
19	Sulfonated Polystyrene <sup>(c)</sup>	Anionic	1.40	46
20	Sulfonated Polystyrene <sup>(c)</sup>	Anionic	1.62	57
21	Sulfonated Polystyrene <sup>(c)</sup>	Anionic	1.63	55
22	90% Acrylamide—10% Sodium Acrylate	Anionic	0.31	32
23	90% Acrylamide—10% Sodium Acrylate	Anionic	0.78	44
24	83% Acrylamide—17% MTMMS	Cationic	0.54	63

(a) p.p.m. dry weight basis by weight of total sewage treated added as a 0.05% aqueous solution.

(b) Based on suspended solids conc. of about 215 p.p.m. and 1 hr. settling time.

(c) Flocculating agent available commercially as "PURIFLOC A-21".

#### EXAMPLES 25—34

##### Laboratory Runs

5 These runs were carried out to determine the effect of various polymeric flocculating agents on the recovery of suspended solids from a mixture of raw sewage and recycle streams which had been aerated.

10 Samples of aqueous sewage were taken from the primary sedimentation tank effluent (overflow) of a sewage plant. This sewage slurry comprised a mixture of the following.

- (1) raw sewage (no previous aeration)
- (2) recycle of effluent (overflow) from a conventional thickener tank employed in the sewage plant, in which thickener tank both the solids in sludge from the primary sedimentation tank, and the solids in a sludge resulting from aeration followed by final sedimentation of the effluent (overflow) from the primary sedimentation tank had been further concentrated to constitute said recycle of

effluent (overflow) and leave a bottoms of concentrated sludge, and (3) recycle effluent (overflow) from an elutriator in the sewage plant. The feed to the elutriator is comprised of the sludge from the thickener tank, which sludge has been digested. One liter of this aqueous sewage mixture was placed in each of several clean 1-liter graduated cylinders. Flocculating agent was then added to the sewage and mixed therewith by inverting the graduated cylinders 10 times, after which the cylinders were allowed to stand for 1 hour. A 50-ml. portion of the supernatant was pipetted from each of the graduated cylinders at the 900-ml. mark and filtered through a weighed glass fiber filter paper having a pore size of 1 micron. The filter paper was oven dried 1 hour at 110°C. and reweighed to determine the per cent solids settled.

Further details appear in Table 3 herein-after.

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TABLE 3

## Laboratory Runs

Effect of Various Polymeric Flocculating Agents on  
Suspended Solids Recovery from a Mixture of Raw  
Sewage and Sewage from Recycle Streams, a Portion  
of which Recycle Sewage had been Aerated

Ex. No.	Flocculating Agent			Per Cent Solids Settled <sup>(b)</sup>
	Name	Type	Amount <sup>(a)</sup>	
25	None	None	None	41
26	Sulfonated Polystyrene <sup>(c)</sup>	Anionic	0.50	20
27	50% Acrylamide—50% Sodium Acrylate	Anionic	0.50	18
28	50% Acrylamide—50% Sodium Acrylate	Anionic	1.50	15
29	90% Acrylamide—10% Sodium Acrylate	Anionic	0.10	21
30	90% Acrylamide—10% Sodium Acrylate	Anionic	1.50	19
31	96% Acrylamide—4% MTMMS	Cationic	0.10	55
32	83% Acrylamide—17% MTMMS	Cationic	0.10	73
33	83% Acrylamide—17% MTMMS	Cationic	1.25	76
34	60% Acrylamide—40% MTMMS	Cationic	0.10	75

(a) p.p.m. dry weight basis by weight of the total sewage treated added as a 0.01% aqueous solution.

(b) Based on suspended solids conc. of 342 p.p.m. and 1 hr. settling time.

(c) Flocculating agent available commercially as "PURIFLOC A-21".

As pointed out hereinbefore there are certain systems wherein the prior art has not only had difficulties with trying to use anionic poly-electrolytes as flocculants and settling aids but wherein a poorer job was done with than without these flocculants, Table 3 above being representative of such systems.

## EXAMPLES 35 AND 36

## Sewage Plant Runs

These runs were carried out to determine the effect of various polymeric flocculating agents on the recovery of suspended solids from the same sewage mixture as in Examples

Flocculating agent was fed into the sewage treatment plant at a point just prior to the flow of raw aqueous sewage slurry into the primary sedimentation tanks into which passed the same recycle streams as set forth in Examples 25—34. Samples were taken from the effluent (overflow) from the primary sedimentation tanks and the per cent solids settled determined from these. The sampling time, i.e. the time between addition of the flocculating agent and making this determination on the thus treated samples, was approximately 1 hour.

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TABLE 4  
Sewage Plant Runs  
Effect of Various Polymeric Flocculating Agents on  
Suspended Solids Recovery from a Mixture of Raw  
Sewage and Sewage from Recycle Streams

Ex. No.	Flocculating Agent			Per Cent Solids Settled <sup>(b)</sup>
	Name	Type	Amount <sup>(a)</sup>	
35	None	None	None	62
36	83% Acrylamide—17% MTMMS	Cationic	0.09	76

(a) p.p.m. dry weight basis by weight of the total sewage treated added as a 0.05% aqueous solution.

(b) Based on suspended solids conc. of about 350 p.p.m. and 1 hr. settling time.

From the foregoing examples it is readily apparent that the particular cationic copolymer flocculating agent used in the present invention, as compared with several typical polymeric flocculating agents of the prior art, gives substantially improved flocculation both from the standpoint of increased rate of flocculation and total amount of suspended solids recovery. The amount of flocculating agent used in the present invention required can also be considerably less than that of the prior art. Very small amounts give substantial improvements in both rate of flocculation and total amount of suspended solids recovery, for instance, as little as 0.10 p.p.m. by weight of the total sewage being treated gave almost twice as much suspended solids recovery as the control (Table 3, Example 34). From 0.05—5 p.p.m., dry weight basis by weight of the sewage treated, of the particular cationic copolymer flocculating agent used in the present invention gives these improvements to a substantial degree. Preferably the amount of copolymer flocculating agent used in accordance with the present invention will be from 0.1—3 p.p.m., dry weight basis by weight of the total sewage treated, 0.1—1 p.p.m. being specifically preferred. Those skilled in the art to which this invention relates will appreciate that sewage systems vary tremendously and that the amount of any given flocculating agent employed will vary accordingly. The foregoing examples were carried out on the same sewage system as shown.

The cationic acrylamide-MTMMS copolymer flocculating agents applicable in the present invention may consist by weight thereof essentially of 99%—20% acrylamide and

1%—80% MTMMS, preferably 97%—50% acrylamide and 3%—50% MTMMS, 95%—60% acrylamide and 5%—40% MTMMS being specifically preferred. Preparation of these cationic acrylamide-MTMMS copolymers applicable herein, and the preparation of the anionic acrylamide-sodium acrylate copolymers employed in the examples hereof and not otherwise identified, are set forth in U.S. patents Nos. 3,336,269 and 3,336,270.

Although the flocculating agent used in accordance with the present invention may be added in dry form to the sewage being treated, it is preferred that it be added as an aqueous solution in order to obtain faster and more complete dispersion thereof throughout the sewage slurry.

#### WHAT WE CLAIM IS:—

1. A process of treating sewage, at least a portion of which has been subjected to aerobic microbial action, which comprises contacting said sewage with an acrylamide-beta-methacryloyloxyethyltrimethylammonium methyl sulfate copolymer, thereby (1) increasing the rate at which suspended solids flocculate and settle out of said sewage, and (2) increasing the amount of suspended solids which flocculate and settle out.

2. The process according to Claim 1 wherein contact is effected by mixing the sewage and the copolymer and then allowing the resulting slurry to settle.

3. The process according to Claim 1 or 2 wherein the amount of said copolymer is from 0.05—5 p.p.m. dry weight basis by weight of the sewage treated.

4. The process according to Claim 1 or 2 wherein the amount of said copolymer is from 0.1—3 p.p.m. dry weight basis by weight of sewage treated.

5. The process according to Claim 1 or 2 wherein the amount of said copolymer is from 0.1—1 p.p.m. dry weight basis by weight of sewage treated.
- 5 6. The process according to any one of the preceding claims wherein said copolymer consists by weight thereof of 99%—20% acrylamide and 1%—80% beta methacryloyloxyethyltrimethylammonium methyl sulfate.
- 10 7. The process according to any one of the Claims 1 to 5 wherein said copolymer consists by weight thereof of 97%—50% acrylamide and 3%—50% beta methacryloyloxyethyltrimethylammonium methyl sulfate.
8. The process according to any one of the Claims 1 to 5 wherein said copolymer consists by weight thereof of 95%—60% acrylamide and 5%—40% beta methacryloyloxyethyltrimethylammonium methyl sulfate. 15
9. The process of treating sewage according to Claim 1 substantially as herein described in the preceding example. 20

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